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**NATURE OF THE PASSIVE FILM ON IRON
IN CONCENTRATED NITRIC ACID**

by

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ABSTRACT

The film responsible for passivity when iron is immersed in concentrated nitric acid is shown to be ferric acid or a related higher valence iron compound. This was proved by (1) demonstrating formation of chromates when a 2.84% Cr-Fe alloy is passivated, (2) by showing complete suppression of the iron-nitric acid reaction when iron is previously immersed in potassium ferrate solution, and (3) by immersing passive iron in NaOH solution and observing higher valence iron compounds displaced from the surface by adsorbed OH^- . The maximum of 2×10^{-8} mole ferric acid per square centimeter that was found is the same order of magnitude as moles chromate adsorbed on iron from chromate solutions as reported by other investigators. This amount of ferric acid, when it decomposes, is calculated to form a film of ferric oxide 40-125 Å thick, which thickness range agrees with that of residual oxide films on passive iron measured previously by others.

The higher valence iron compound forms at anodic areas of the iron surface during the iron-nitric acid reaction. When sufficient local concentration is achieved, the compound adsorbs (chemisorbs) on iron, satisfies metal surface affinities, and is itself stabilized against

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In a previous paper⁽¹⁾, several experiments on passivation of evaporated

⁽¹⁾H. C. Gatos and H. H. Uhlig, J. Electrochem. Soc., 99, 250-258 (1952).

iron films established that a certain amount of iron reacts rapidly with concentrated HNO_3 before the reaction is retarded. Pre-exposure of the iron films to oxygen, carbon monoxide or dilute potassium dichromate solution appreciably reduced the initial amount of iron reacting. This was explained in terms of local action currents on the iron surface serving to polarize anodic areas. The above substances adsorbed on iron increase the effective cathodic area thereby increasing the anodic current density. It was observed, correspondingly, that external anodic polarization of iron in nitric acid decreased the amount of iron reacting before passivation. Continued investigation along similar lines is reported herewith. These results, combined with important contributions to the subject by Bonhoeffer and co-workers⁽²⁾, provide a clearer

⁽²⁾K. F. Bonhoeffer, Zeit. f. Metallkunde, 44, 77 (1953).
(This paper summarizes many earlier papers.)

interpretation of the passivation mechanism by nitric acid than has been available heretofore. The process apparently is not so simple as

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the formation of a barrier film of ferric oxide.

Experimental Procedure

The experimental techniques were essentially the same as those employed by Gatos⁽¹⁾. Two types of iron surfaces were utilized; in one case by evaporation of iron onto glass, and in the other by employing Armco iron foil. The evaporated films were prepared by heating in vacuum either pure iron wires of 0.040-inch diameter, or by wrapping iron wire on electrically heated tungsten filaments of 0.025-inch diameter. The iron vapor was condensed on slowly rotating glass cylinders 35 mm long and 4 mm in diameter. The coated cylinders were then removed magnetically from the evaporation chamber and sealed off in glass tubes, or when surface area determinations were made, the cylinders were transferred to another portion of the vacuum system through glass tube conduits without exposure to air.

Absolute surface area measurements were made on a number of such films by the B.E.T. Method⁽³⁾ in which ethane was adsorbed on the metal

⁽³⁾S. Brunauer, P. Emmett and E. Teller, J.A.C.S., 59, 2682 (1937).

at liquid oxygen temperatures (-183°C). Use of ethane permitted surface area measurements on specimens having as little as 100 cm^2 of absolute surface. It was found that relatively smooth films of roughness factor 1.7 were obtained from iron-wrapped tungsten wires, whereas films of greater absolute surface were formed by evaporation from iron filaments (roughness factor = 5 to 11). Apparently, the lower deposition temperatures using iron filaments retarded sintering of the condensed film, resulting in an irregular array of crystals and perhaps a porous structure. These

films of higher roughness factors were used only in comparison experiments, the majority of the data being obtained with the smoother films.

The Armco foil specimens were generally 3 x 3 cm and 0.0075 cm thick. After preliminary degreasing in boiling benzene, they were pickled for 2 minutes in 15% HCl at 100°C (210°F), washed, and immersed successively into boiling acetone and boiling benzene. Specimens before use were aged in a desiccator overnight; reproducibility was thereby improved probably by allowing escape of interstitial hydrogen absorbed during the pickling operation.

It was necessary to bring the iron-coated glass cylinders into contact with concentrated nitric acid without contamination by exposure to the atmosphere. This was done by inscribing a circumferential scratch on the glass tube in which the iron-coated cylinder was contained, and placing the tube into an "H" shaped glass holder of proper dimensions at the bottom of a beaker of concentrated nitric acid. Using a glass rod, pressure was applied sufficient to break the tube and bring the acid into rapid contact with the iron film. In some experiments, the evacuated specimen tube was broken inside a nitrogen-filled test box fitted with rubber gloves, and the specimen quickly immersed into nitric acid. Films exposed a short time to nitrogen behaved the same as those retained in vacuum.

The nitric acid was purified by distillation in an all-Pyrex still to remove small but annoying traces of iron. Immediately before use, the distilled acid was freed of dissolved oxides of nitrogen by bubbling through gaseous nitrogen for one or more hours. This operation was necessary because of the significant effect of nitrogen oxides on the passivation reaction. The specific gravity of the distilled acid was 1.43 ± 0.005 at ~~15°C (59°F)~~.

15.6°C (60°F)

The amount of iron reacting with nitric acid previous to passivation* was analyzed colorimetrically using the ortho-phenanthroline method. The nitric acid solutions were evaporated to dryness, the residues taken up in 1:1 HCl, and iron determined using an electrophotometer according to the method described by Sandell⁽⁴⁾. This method was considered an

⁽⁴⁾"Colorimetric Determination of Traces of Metals", E. B. Sandell, p. 378, Interscience Pub. Co., New York, 1950.

improvement over the KSCN colorimetric method used by Gatos.

Chromium, in the hexavalent state, was determined colorimetrically using di-phenylcarbazide. The method was essentially that described by Sandell⁽⁵⁾, except nitric acid was used instead of sulphuric acid to

⁽⁵⁾Ref. 4, p. 260, 265

provide the required acidity for development of a violet color. Total chromium was obtained by the same method after oxidation of Cr^{3+} to Cr^{6+} with hydrogen peroxide in dilute alkali. For both iron and chromium analyses, appropriate standards were prepared in solutions of the same kind as those common to the passivation experiments.

Effect of Oxygen Pre-exposure

Exposure of evaporated iron films to oxygen for 30 minutes or longer was found previously to reduce, by approximately one half, the amount of iron reacting with nitric acid before passivity was established. This was confirmed by the present series of experiments (Table I). The next step was to determine minimum partial pressure of oxygen at which

*Time of immersion, 2 minutes, was not critical.

TABLE I

EFFECT OF SOURCE OF IRON, N₂ AND O₂ EXPOSURE, AND ABSOLUTE SURFACE AREA ON AMOUNT OF IRON REACTING WITH HNO₃. Sp. Gr. 1.45

Area of evaporated iron film on glass = approx. 4.2 cm²

Source of Iron	Number of Films Tested	Original Film Thickness* A	Exposure of Film before Reaction	Mg Fe Reacted per sq. cm. geometric area
Nat. Bur. Stds.	10	1700 to 2680	vacuum	0.092±0.019
Westinghouse (Puron)	13	2320 to 3400	vacuum	0.095±0.013
Mallinckrodt	5	2350 to 2400	vacuum	0.090±0.006
Westinghouse (Puron)	5	1980 to 4330 (Roughness factor = 8.7 to 10.8)**	vacuum	0.108±0.012
"	9	1940 to 2500	1 atm. O ₂ , 30 min.	0.04 0.10 ±0.008
"	8	Approx. 2000	1 atm. O ₂ , 30 min. Subsequent evacuation	0.043±0.011
"	6	" "	1 atm. N ₂ for 1 min.	0.091±0.019

*Based on total amount of evaporated iron (density = 7.86), and geometric area.

**Roughness factor for other films listed in this table is approximately 1.7.

the effect is observed. Evaporated films of iron on glass cylinders were allowed to remain in the glass evaporation system, and were then exposed to oxygen at various pressures for a total of 1/2 hour. Adjustment of pressure to the required value necessitated an additional preliminary time of 15 to 30 minutes. After exposure, specimens were sealed off in glass tubes and immersed directly into nitric acid by breaking the container under acid as described previously. Analyses for iron as a function of the oxygen pressure to which the films were exposed are plotted in Fig. 1. There is a gradual trend from the maximum amount of reacted iron for films retained in vacuum, to about one half this value for films exposed to 1 atm. O_2 . The scatter of data is typical of passivation phenomena, and is not unexpected. No critical pressure of oxygen was found, but instead a trend toward lesser amounts of iron reacting as the pressure of oxygen was increased.

Further tests showed that the effect of oxygen at 1 atm. can also be achieved at lower pressures if time of exposure is prolonged. Three films exposed to 2.7×10^{-4} mm oxygen for 24 hours and then reacted with nitric acid in the usual way gave values of 0.055, 0.054 and 0.067 (average 0.058) mg Fe/cm², which can be compared with the value of 0.040 mg Fe/cm² after exposure to 1 atm. O_2 for 30 minutes. Two films sealed off after six hours exposure at 4×10^{-3} mm O_2 pressure produced 0.047 and 0.059 (average 0.053) mg Fe/cm². Oxygen apparently chemisorbs on iron more rapidly the higher the external pressure. Hackerman and Antes⁽⁶⁾ came to the same conclusion through Volta potential measure-

⁽⁶⁾ N. Hackerman and L. Antes, Science, 112, 471 (1950).

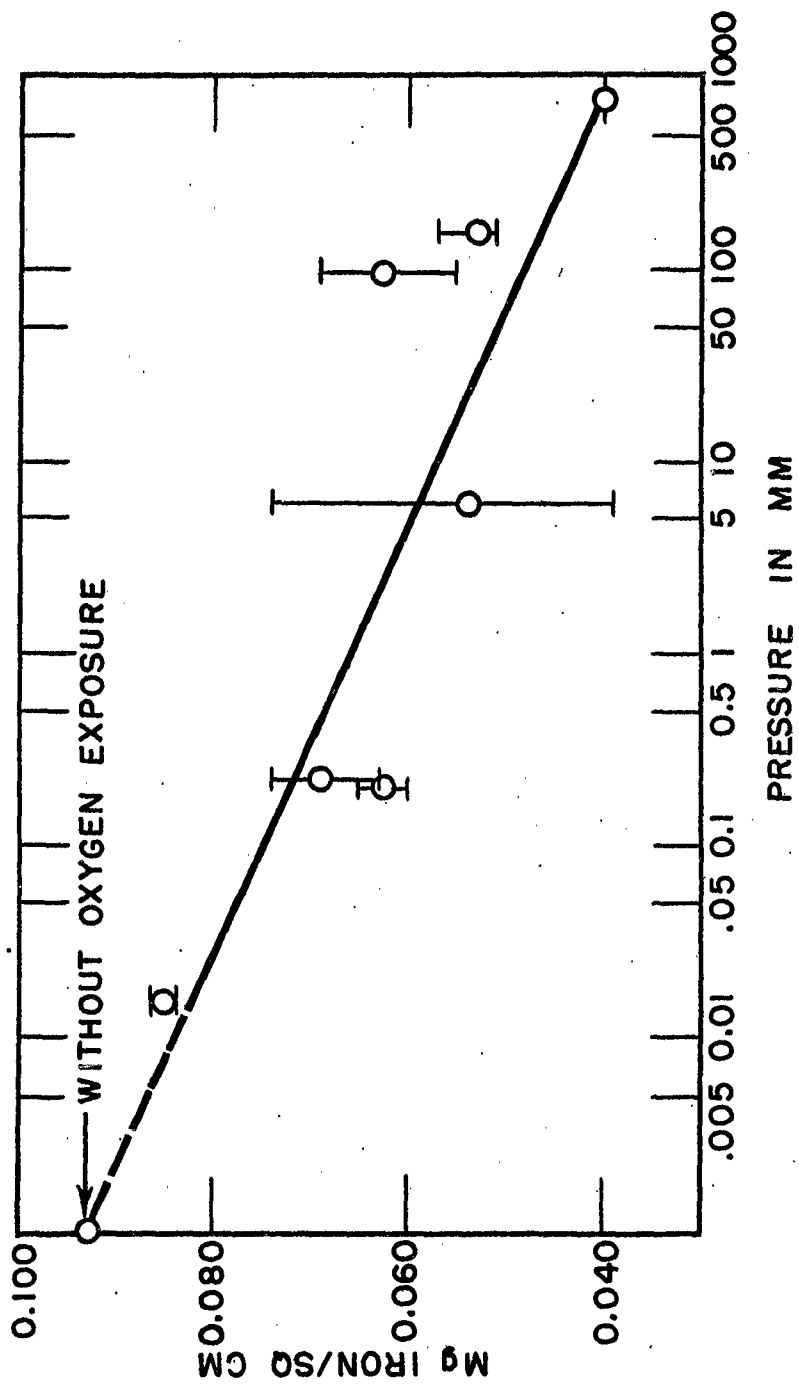


Figure 1 AMOUNT OF IRON REACTING IN NITRIC ACID AFTER EXPOSURE TO OXYGEN AT VARIOUS PRESSURES FOR 1/2 HOUR

ments of iron films exposed to oxygen at various pressures. It is also possible that rate of oxidation of iron to iron oxide increases with O_2 pressure.

Effect of Subsequent Evacuation

After exposure of several films to 1 atm. of oxygen for 1/2 hour, the system was evacuated to 10^{-6} mm pressure for periods ranging from 4 to 12 hours. These films on immersion in nitric acid reacted to the same extent as did those not subject to evacuation after exposure to oxygen. In other words, the effects of oxygen exposure were not removed by evacuation. Data for eight different films gave an average value of 0.043 ± 0.011 mg Fe/cm² (Table I), which compares with the average value for nine films exposed similarly to oxygen but not evacuated, of 0.040 ± 0.008 mg Fe/cm². These measurements can be taken as evidence that effects of oxygen at 1 atm. after 30 minutes contact with iron cannot be removed from the surface by subsequent lowering of the pressure.

Independent measurements of oxygen adsorption on iron films confirmed that the gas is irreversibly adsorbed. These measurements, to be reported in detail elsewhere, showed that adsorption of oxygen proceeds at a high rate initially, followed by a slow rate after a certain amount of oxygen covers the surface. Several iron films were exposed to oxygen at a final pressure of 1.8 to 7×10^{-3} mm Hg pressure for 1 to 5 hours, and were then evacuated at less than 10^{-6} mm Hg pressure for 5 to 12 hours. Oxygen was then allowed again to adsorb on the surface, but the observed rate of adsorption was always low and not characteristic of the high initial rate for a clean iron surface. Failure to regenerate the initial high rate of adsorption is proof that the original surface of

iron is not regained by evacuation. A further check was made by adsorbing 17.4 cc-mm (9.4×10^{-7} mole) oxygen at a final pressure of 3.6×10^{-3} mm, and allowing the gas (17 ml) in contact with 167 cm^2 ^{iron} / (absolute surface) to expand into a known volume (428 ml). The calculated final pressure (0.14×10^{-3} mm), assuming no release of previously adsorbed gas on iron, checked the observed pressure (0.13×10^{-3} mm). Armbruster and Austin⁽⁷⁾ also reported that oxygen is irreversibly adsorbed on iron at

⁽⁷⁾ M. Armbruster and J. Austin, J.A.C.S., 68, 1347 (1946).

room temperature.

The foregoing effects of evacuation on passivity differ from the previous observations by Gatos and Uhlig who reported that the effects of oxygen exposure were removable by pumping out the system. Detailed scrutiny and careful examination of all the facts revealed no certain reason for the discrepancy, but it is possible that the method they used to introduce oxygen-exposed specimens into the acid was at fault. This was done by heating one end of the glass tube and plunging it into acid, whereupon the tube fractured by thermal shock. If in so doing the iron films were heated unintentionally, the effect of oxygen would have been erased as Freundlich et al showed⁽⁸⁾, and with whose results

⁽⁸⁾ H. Freundlich, G. Patscheke and H. Zocher, Z. Physik. Chem., 128, 321 (1927).

our present experiments are now in accord. Heating converts adsorbed oxygen to iron oxide (or, alternatively, the iron oxide film is sintered) which is not as effective a cathode as the adsorbed gas

(or the initial oxide), and, hence, larger amounts of iron dissolve subsequently in the passivation reaction.

The present results otherwise are in qualitative agreement with those reported earlier, including the indifferent effect of pre-exposure to nitrogen (Table I). Quantitatively, the amounts of iron reported per unit area for our present experiments are roughly one half those reported by Gatos and Uhlig. The differences were not found to be caused by variation of true surface area or source of iron, as summarized data of Table I show. The main factor appeared to be the present adoption of an improved method of analysis for small amounts of iron. This method required evaporation of numerous nitric acid solutions to dryness, hence was tedious and extremely corrosive to adjacent equipment. Nevertheless, the accuracy of results was much better than omitting evaporation, both because the concentrated acid no longer interfered with the color reaction, and because the possible size of sample for analysis was inherently larger. It is felt, therefore, that the present values for iron are more nearly correct.

Additions to Nitric Acid

Gatos reported that exposure of iron films to oxygen-saturated 0.1% $K_2Cr_2O_7$ reduced the amount of iron reacting with concentrated nitric acid as time of exposure increased, with very little or no iron reacting for exposures greater than 30 minutes. This was confirmed by the present series of experiments using two evaporated iron films, three hydrogen-reduced Armco foil specimens, and four pickled Armco foil specimens. Each was pre-exposed 45 minutes to 0.1% $K_2Cr_2O_7$, and the excess solution

drained off on filter paper before immediate immersion into nitric acid. For all specimens, the weight loss on passivation was 0.000 ± 0.001 mg/cm². In other words, pre-exposure of iron to dilute chromate solutions completely passivates it with respect to reaction with concentrated nitric acid.

Addition of potassium dichromate directly to nitric acid was found to accomplish the same thing, although the concentration required was higher than 0.1%. Armco foil specimens were used, previously pickled in 15% HCl at 100°C for two minutes, and allowed to age in a desiccator overnight. Data are plotted in Fig. 2. There is no effect on the reaction by dissolved chromate up to 0.1 gm/50 ml acid (2 gms K₂Cr₂O₇/liter). The higher value for reacted iron using Armco foil (0.07 mg/cm²) than for evaporated films (0.04 mg/cm²) may be caused by the increased absolute surface of the HCl pickled specimens, and also probably reflects a greater accumulation of air-formed iron oxide film which dissolves during the passivation treatment and adds to the iron in solution. A rather sudden reduction in reaction rate occurs between 0.1 and 0.5 gm K₂Cr₂O₇/50 ml nitric acid (2 to 10 gms K₂Cr₂O₇/liter), and the rate remains essentially zero for higher concentrations. The data indicate, therefore, that the passivating effect of chromates can be induced either by pre-exposure of iron to dilute solutions of chromates for a sufficient time, or by adding chromates directly to the nitric acid.

Similar experiments were carried out with addition of potassium nitrite to the acid (Fig. 3). The liberation of nitrous acid has an appreciable effect on the amount of iron reacting when the KNO₂ concen-

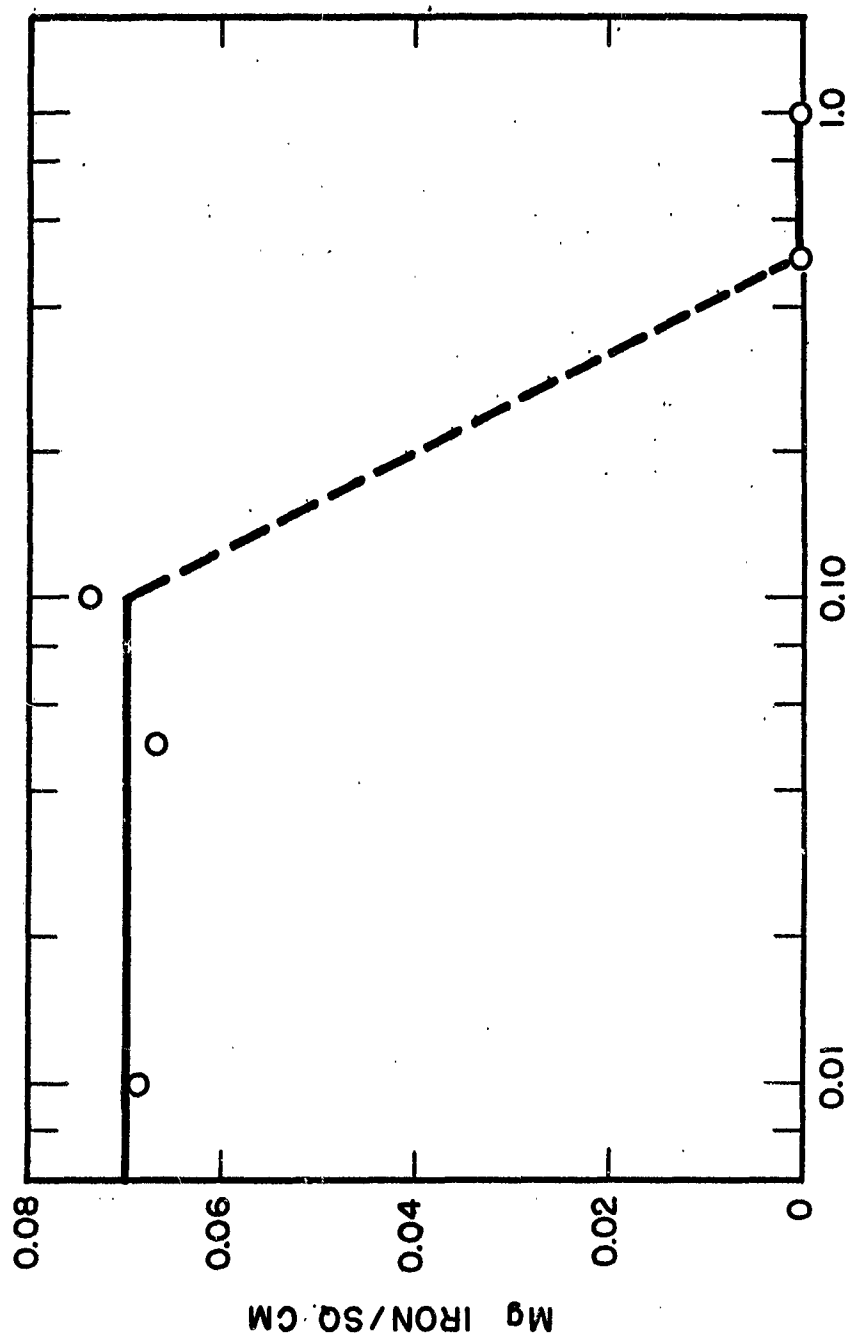


Figure 2 EFFECT OF ADDITION OF $K_2Cr_2O_7$ TO NITRIC ACID (S.G. 1.43)
ON AMOUNT OF IRON REACTING

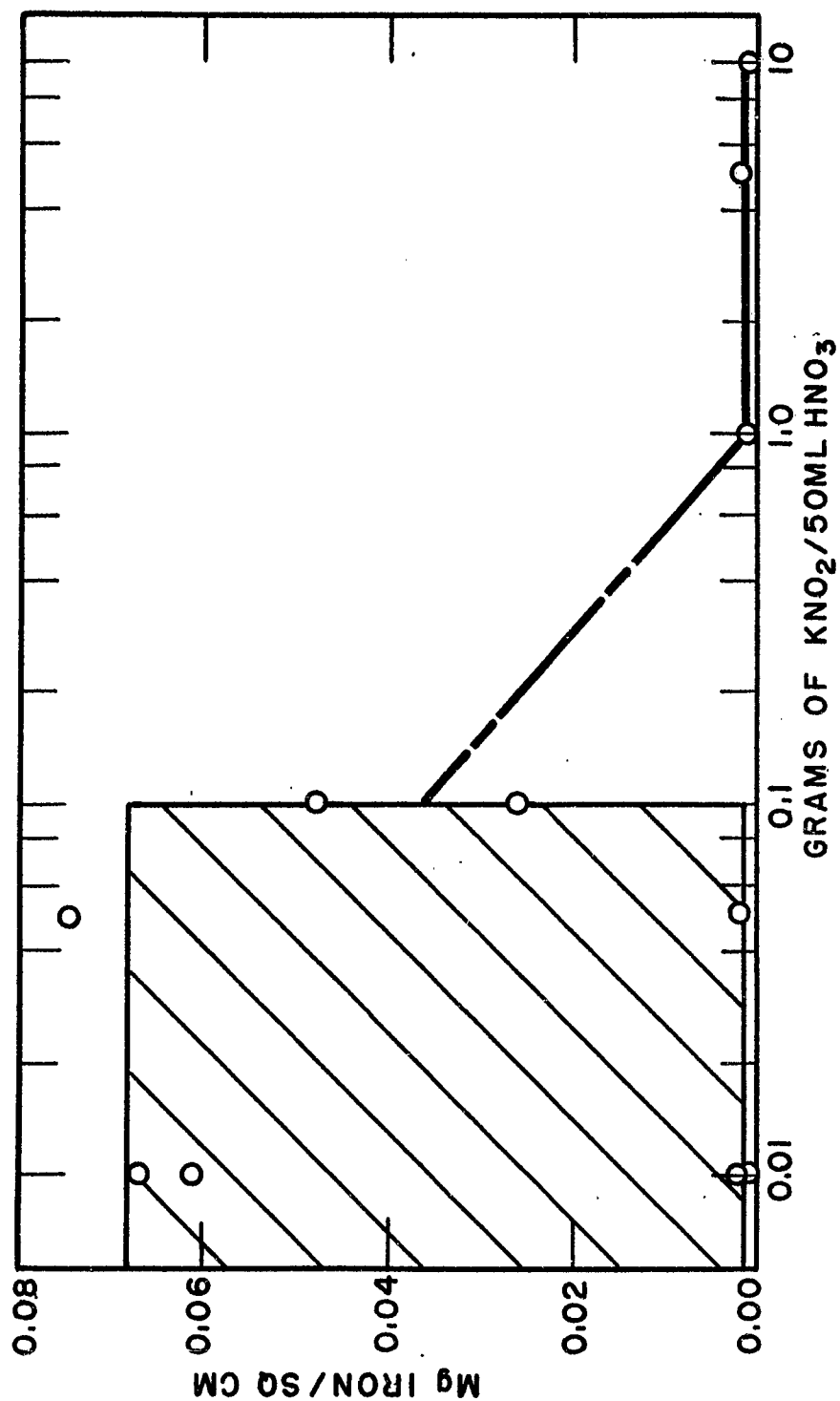


Figure 3 EFFECT OF ADDITION OF KNO₂ TO NITRIC ACID (S.G. 1.43) ON AMOUNT OF IRON REACTING

tration is over 0.1 gm/50 ml HNO_3 (2 gms/liter). Below this concentration, the effects are erratic, with either the usual amount of iron reacting, as when nitrites are absent, or almost none reacting as is uniformly true of concentrations over 0.1 gm KNO_2 /50 ml acid. It is important to note, from the standpoint of mechanism discussed later, that the average amount of iron reacting in acid containing more than the critical amount of dichromate or nitrite was essentially 0.000 mg Fe/cm² for dichromate (5 determinations), but measurably higher for nitrite, namely 0.0013 mg Fe/cm² (8 determinations).

The obvious importance of nitrous acid or its decomposition products to the passivation reaction suggested adding substances capable of reaction with HNO_2 and which reduce its concentration. Urea is one such substance, which is stated⁽⁹⁾ to react as follows:



⁽⁹⁾"Inorganic Chemistry", F. Ephraim, Transl. by P. Thorne and A. Ward, p. 684, Gurney and Jackson (London) 1939.

The reaction products have also been stated to include cyanic acid, HCNO .

According to Vetter⁽¹⁰⁾, an excess of urea reduces the ultimate

⁽¹⁰⁾K. Vetter, Z. Elektrochem., 55, 274 (1951).

concentration of nitrous acid in nitric acid to about 1×10^{-5} moles/liter.

Fig. 4 shows that below 0.5 gm urea/50 ml HNO_3 , the iron was passivated with approximately the usual amount of iron reacting. Even with as little as 0.01 gm urea, however, no color developed in the acid, and considerable gas was evolved showing that urea was effective in removing the nitrous acid. At the highest concentration or 1.0 gm urea/50 ml, HNO_3 , which approached the solubility of urea in the acid, approximately twice as much iron reacted as for smaller concentrations. In the latter solution, however, iron was only passive temporarily, with periods of passivity alternating with periods of activity. Naturally, more iron reacts under these conditions than when passivity is stable over the usual two-minute period of immersion in the acid.

Addition of hydrogen peroxide showed a more marked effect on the amount of iron reacting. Data are plotted in Fig. 5, each point representing an average of two determinations. As in the case of urea, the effect was accompanied by periodic breakdown and re-formation of the passive state, each cycle being attended by dissolution of iron. The higher the concentration of H_2O_2 , the more rapid was the frequency of breakdown. The effect observed is not one of dilution, because addition of water equivalent to that added with hydrogen peroxide showed only a small effect (Fig. 5).

Formation of Higher Valence Compound

The facts thus far provided evidence that $\text{K}_2\text{Cr}_2\text{O}_7$ either on the surface of iron or in nitric acid substantially reduces attack of iron during the passivation reaction. Potassium nitrite added to nitric acid also reduces the attack, with an effect slightly less than for

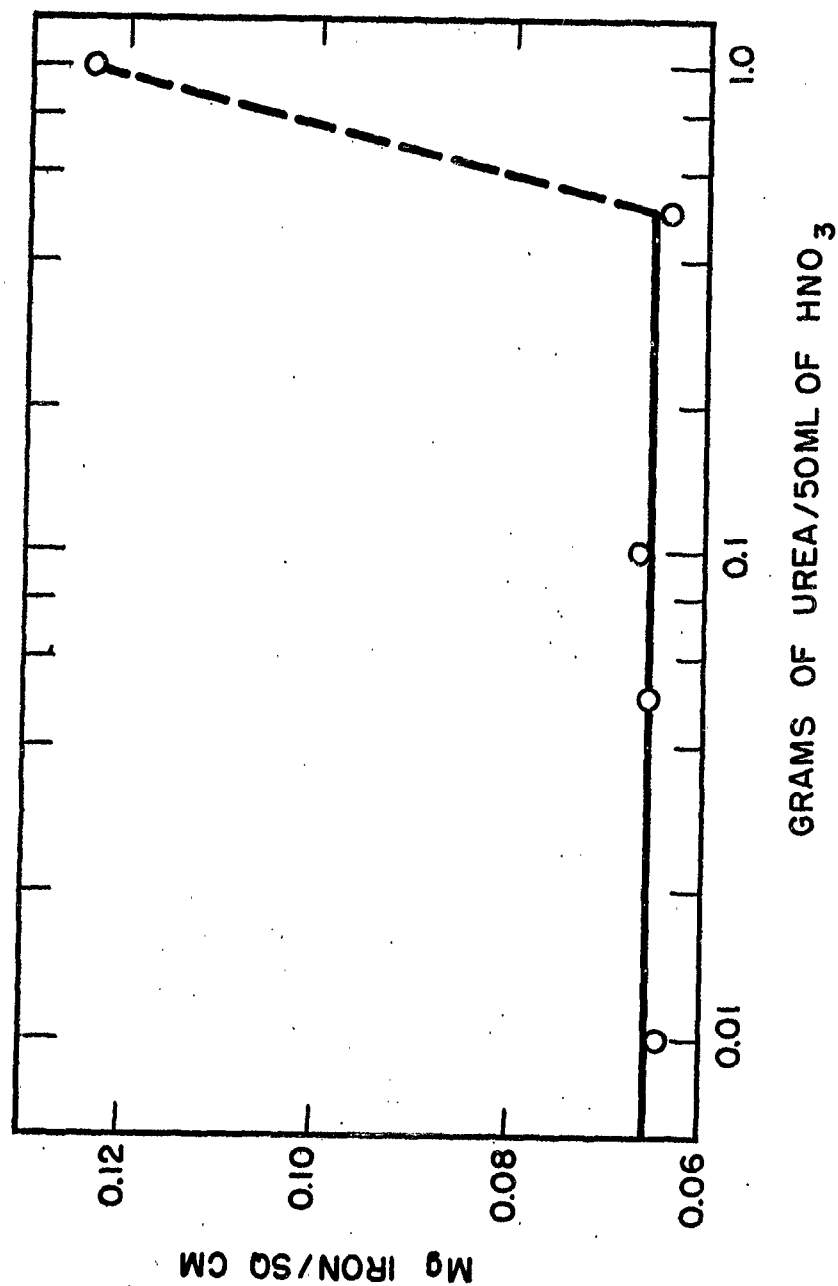


Figure 4 EFFECT OF ADDITION OF UREA TO NITRIC ACID (S.G. 1.43)
ON AMOUNT OF IRON REACTING

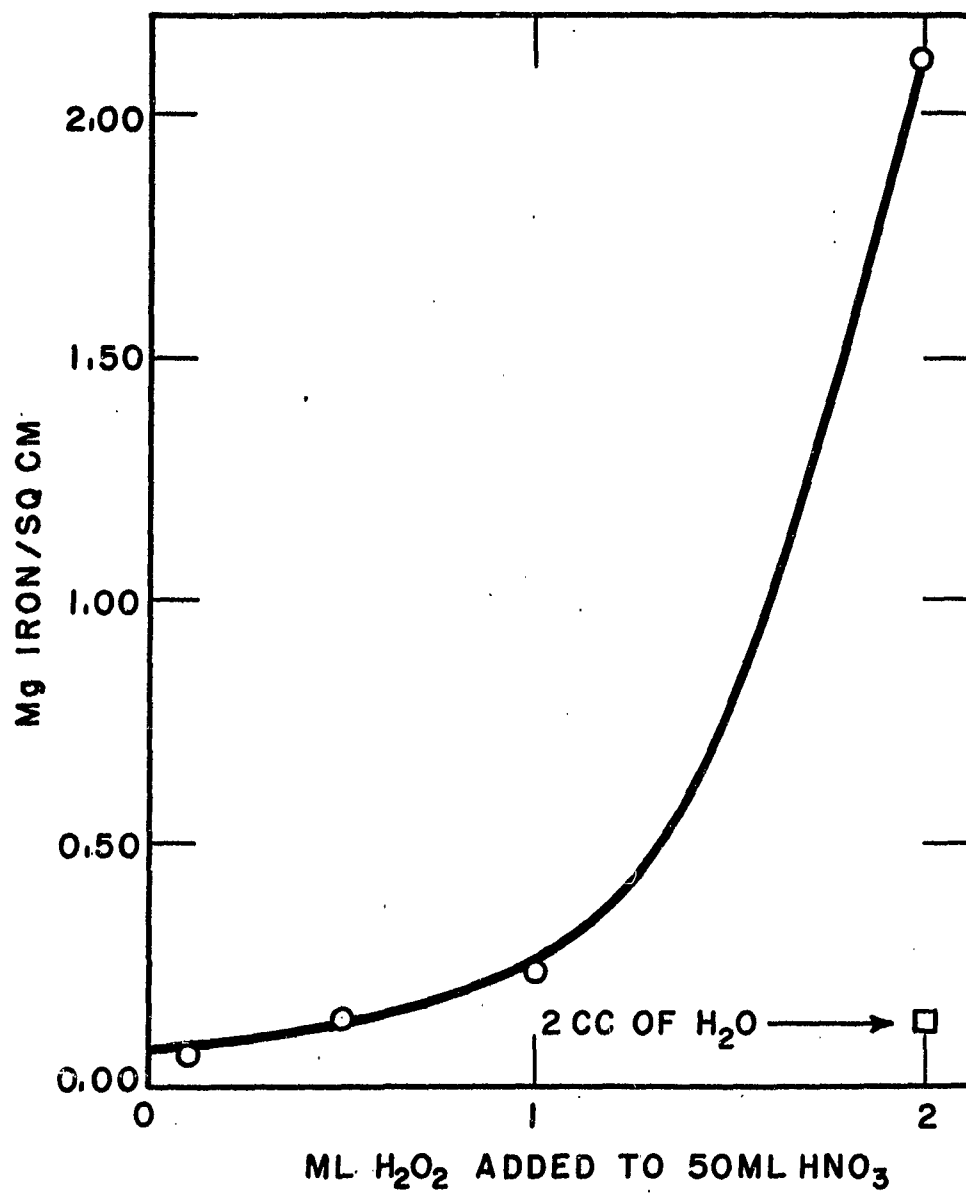


Figure 5 EFFECT OF ADDITION OF 30% HYDROGEN PEROXIDE ON THE AMOUNT OF Fe REACTING IN NITRIC ACID (S.G. 1.43)

dichromate. Further experiments showed that pre-exposure of iron to saturated nitrite solution for 1 hour followed by washing in water had no measurable effect on the amount of iron reacting with nitric acid, contrary to similar pre-exposure to dichromate. Potential measurements in distilled water of iron wires (0.040 inch diameter, sealed in lead glass) previously passivated either in concentrated HNO_3 or in 0.1% K_2FeO_4 and washed in water, were of the same order initially, namely 0.9-1.0 volt on the normal hydrogen scale. It seemed reasonable, therefore, to hypothesize the formation of a compound during the iron-nitric acid reaction similar in structure and properties to ferric acid, H_2FeO_4 , as the key substance responsible for passivity. Any of the normal oxides of iron cannot account for the observed noble potential, as Bonhoeffer⁽²⁾ showed. Although ferric acid is unstable when dissolved in acids, its rate of decomposition is probably retarded when it is adsorbed on iron.

To check the role of ferric acid, potassium ferrate was prepared, in accord with a method described by Thompson, Ockerman and Schreyer⁽¹¹⁾.

⁽¹¹⁾ G. Thompson, L. Ockerman and J. Schreyer, J.A.C.S., 73, 1379 (1951).

Exposure of Armco iron specimens to freshly dissolved 0.1% solution* for 45 minutes, draining of excess ferrate solution onto filter paper, and immersion of the specimen into nitric acid in the usual way showed indeed that iron was protected from reaction with nitric acid in the same manner as was provided by pre-exposure to dichromate solutions. A small amount

*The solution decomposed slowly, but the purple color of ferrate was still visible at the end of 1 hour.

of iron was found in nitric acid after immersion (0.003 and 0.002 mg Fe/cm² in two experiments), which is accounted for by residual ferrate solution adhering to the iron surface. It was not possible, of course, to check the effect of ferrate added directly to nitric acid as was done with chromate because of the instability of the compound in acid solutions.

The next experiments were directed toward detection of hexavalent iron compounds possibly formed in the passivation reaction. The transient nature of such compounds and their obviously small concentration at any time during the reaction made the task difficult. However, since chromates are relatively stable, and conditions for their formation are reasonably parallel to those for hexavalent iron compounds, it was decided to use a small amount of alloyed chromium in iron as a tracer element. Accordingly, specimens of a laboratory-prepared melt of 2.84% Cr-Fe alloy were fabricated into sheet specimens each having a total geometric area of about 6 cm². This alloy, immersed in concentrated nitric acid for 2 minutes, lost 0.025 mg/cm², which is about one third the value, 0.07 mg/cm², for pure iron. (Higher chromium alloys corroded still less.)

Because iron interfered to some extent with analyses for chromium using the di-phenyl carbazide color reaction, the solution was made alkaline to pH 8, and the ferric hydroxide centrifuged off. A calibration curve was constructed using weighed amounts of K₂Cr₂O₇ in concentrated HNO₃. Total chromium, when required, was determined by first oxidizing Cr³⁺ to Cr⁶⁺ in dilute alkali using H₂O₂.

The first experiments involved successively passivating the 2.8% Cr-Fe alloy for a total of 100 times in 50 ml of concentrated HNO₃,

activating the specimen each time in dilute HCl followed by thorough washing in distilled water. Large amounts of oxides of nitrogen were generated in the nitric acid, and the passivating reaction each time was characterized by a dark reddish-brown film creeping over the alloy surface. Careful analysis of the acid revealed complete absence of hexavalent chromium, with the analytical method estimated to be sensitive to about 50 micrograms of dichromate. The test was repeated using cathodic activation of the specimen in water so as to avoid possibility of contamination by chloride ion, but with the same result.

The next experiment was the anodic polarization of the alloy specimen (5.6 cm^2) in 3% Na_2SO_4 for one hour at a current density of 40 ma/cm^2 . Oxygen was evolved over all the surface of the anode indicating that the alloy was passive, and slight precipitation of ferric hydroxide within the solution revealed some metal dissolution in addition. The anodic corrosion accounted for 1% of the total electricity passing through the cell. In this instance chromate was found, and, furthermore, all the chromium going into solution was hexavalent. Data for this and the following few experiments are summarized in Table II.

The third experiment consisted of anodically polarizing the alloy in concentrated nitric acid again for 1 hour at 40 ma/cm^2 . There was more anodic corrosion than before, about 65% of the current representing anodic dissolution compared with 1% for Na_2SO_4 . No dichromate, however, was detected.

TABLE II

ANALYSIS OF CORROSION PRODUCTS OF PASSIVATED 2.8% Cr-Fe ALLOY

Passivation Treatment	Total Metal in Solution		Cr ₂ O ₃ found, mg	Current Efficiency for Fe $\xrightarrow{+++}$ Fe ⁺⁺⁺ + 3e
	Cr, mg	Fe, mg		
1. HNO ₃ 100X, HCl activation	1.30	---	0.0	---
2. HNO ₃ 50X, cathodic activation	0.63	29.2	0.0	---
3. Anodic Polarization 3% Na ₂ SO ₄ 40 ma/cm ² , 1 hour	0.046	1.6	0.095	1%
4. Anodic Polarization, HNO ₃ 40 ma/cm ² , 1 hour	2.4	98.7	0.0	63%
5. Anodic Polarization HNO ₃ 40 ma/cm ² , 1/2 hour, H cell	1.5	57.0	1.6	67%
6. Same as 4, HNO ₃ saturated with urea, 1/2 hour.				
a. Analysis for Cr ⁶⁺ immediately	1.21	53.0	0.36	63%
b. " " 2½ hours after electrolysis	---	---	0.25	---
c. " " 12 hours after electrolysis	---	---	0.0	---
7. HNO ₃ saturated with urea, 50X, cathodic activation	0.62	---	0.0	---

The difference in results, depending on electrolyte, suggested that hexavalent chromium in nitric acid was probably being reduced by cathodic reduction products freely circulating throughout the volume of acid. In Na_2SO_4 , the cathodic products are H_2 and NaOH , the hydrogen escaping from the solution, but in nitric acid, products such as nitrous acid remain in solution. It was found, in accord with this reasoning, that small quantities of potassium nitrite added to concentrated HNO_3 containing dissolved $\text{K}_2\text{Cr}_2\text{O}_7$ completely reduced the dichromate, as determined by analysis. In other words, dichromate rapidly oxidizes nitrous acid (Table III).

The fourth experiment, therefore, was to repeat the foregoing experiment, but with separation of anolyte and catholyte in an H-type cell with a fritted glass disc separating the two compartments. In addition, a stream of nitrogen was passed through both compartments to remove any oxides of nitrogen from solution.

Using this arrangement with a current density of 40 ma/cm^2 for 30 minutes (area anode = 6.1 cm^2), analysis of the anolyte now revealed positive presence of dichromates, with a current efficiency for anodic dissolution remaining at about 50%. In absence of reducing agents, therefore, hexavalent chromium is formed on anodic polarization of the 2.8% Cr-Fe alloy in nitric acid.

The fifth experiment involved the addition of urea to concentrated nitric acid which, as noted previously, reacts with nitrous acid and greatly reduces its concentration. Using the electrolytic cell without separation of anolyte and catholyte, dichromates this time were found. The amount of dichromate decreased with time after electrolysis was dis-

TABLE III

REDUCTION OF $K_2Cr_2O_7$ IN CONCENTRATED HNO_3 BY ADDITIONS OF KNO_2

<u>gm KNO_2 added to 50 ml HNO_3 + 0.41 ppm $Cr_2O_7^{--}$</u>	<u>ppm $Cr_2O_7^{--}$ found by analysis</u>
0.10	0.0
0.05	0.0
0.01	0.0
0.0	0.42
0.0	0.39

continued, as data of Table II show, probably because urea is oxidized slowly by dichromates. This, plus the fact that some nitrous acid is present, also explains the smaller quantity of Cr_2O_7 found compared with experiment 5. However, in absence of anodic polarization, and by merely dipping the specimen 50 times into the urea-nitric acid mixture, activating the specimen cathodically in water each time, no dichromate was found (Exp. 7, Table II). Apparently, the dichromate under these conditions is reduced by ~~cathodic products~~ HNO_2 , formed in close proximity to the anodes, more rapidly than urea can diffuse to the metal surface and react with HNO_2 . Vetter⁽¹⁰⁾ has shown, for example, that it requires approximately 1 minute for a 1% solution of urea in concentrated HNO_3 to reduce the nitrite concentration from 4×10^{-3} to 1×10^{-4} mole/liter.

Detection of Hexavalent Iron Compound

With definite formation of dichromates on anodic polarization of the Cr-Fe alloy in nitric acid, the next question concerned the analogous formation of a hexavalent iron compound and its similar properties as a passivator. This question previously had been answered in part by pre-exposing iron to dilute potassium ferrate or to potassium chromate, and observing in either instance the complete suppression of reaction with nitric acid.

Evidence from the potential behavior of iron in various chromate solutions indicated that the Langmuir adsorption isotherm is obeyed⁽¹²⁾,

⁽¹²⁾ H. H. Uhlig and A. Geary, J. Electrochem. Soc., 101, 215 (1954).

confirming that passivation by chromates is accompanied by their

adsorption on iron, as had been suggested earlier⁽¹³⁾. Radioactive

⁽¹³⁾H. H. Uhlig, Chem. Eng. News, 24, 3154 (1946).

tracer studies⁽¹⁴⁾ on the amount of radioactive chromium on the surface

⁽¹⁴⁾D. Brasher and E. Stove, Chem. and Industry, 171, No. 8 (1952).

of iron as a function of chromate concentration also showed that an approximate adsorption isotherm is followed. Evidence for adsorption accompanying passivation was also reported by Powers and Hackerman⁽¹⁵⁾.

⁽¹⁵⁾R. Powers and N. Hackerman, J. Electrochem. Soc., 100, 314 (1953).

They showed that chromates were adsorbed on iron below pH 11 and could not be washed off (chemisorption), whereas above pH 11 chromates were not adsorbed at all. These facts immediately suggested that hexavalent iron compounds analogously may adsorb on iron. Furthermore, if they are the cause of passivity in nitric acid, they should be released from the metal surface by immersing passive iron in strong alkalies, and, in the case of iron containing alloyed chromium as tracer, some chromates should be released simultaneously.

The next experiment, therefore, was to passivate the 2.84% Cr-Fe alloy (6.1 cm² area) in concentrated HNO₃, wash in water, immerse in 2 N NaOH, then in dilute HCl, and again wash in distilled H₂O, repeating this procedure successively 50 times. Analysis of the sodium hydroxide solution, carrying out this procedure, showed indeed the presence of 53 micrograms of Na₂CrO₄. Repetition of the same procedure using HCl

instead of HNO_3 did not passivate iron and correspondingly produced no detectable amount of chromate. This experiment proved, therefore, that hexavalent chromium forms when the chromium-iron alloy is passivated in concentrated nitric acid, and furnishes strong evidence that the chromates so formed are in part chemisorbed.

Formation of Hexavalent Iron Compounds in Nitric Acid

With the preceding evidence for hexavalent chromium, a cell was set up to demonstrate the possibility that hexavalent iron can form by the nitric acid-iron reaction. To one compartment of an H-type cell, 5 N NaOH was added in contact with an Armco iron electrode (2 x 2 cm), and concentrated HNO_3 was added to the other compartment in contact with a platinum electrode of similar size. On electrically short circuiting the two electrodes, light purple reaction products, characteristic of sodium ferrate and exhibiting typical oxidation reactions, streamed off the iron accompanied by oxygen evolution. A similar experiment was repeated using 0.1 N NaOH instead of the more concentrated alkali with identical although less pronounced results. By employing 3% Na_2SO_4 instead of NaOH, however, no ferrate formed visibly, oxygen being the only observable anodic product. In a solution such as this, it is probable that if ferrate is formed, it is immediately adsorbed on the electrode surface with no tendency for its release, whereas in NaOH the hydroxyl ion adsorbs preferably and continuously displaces ferrate ions.

It remained to demonstrate that the compound formed on pure iron and displaced by hydroxyl ions has oxidizing properties typical of

ferrates. Analysis of the suspected compound was based on a method described by Schreyer, Thompson and Ockerman⁽¹⁶⁾. To 20 ml saturated

⁽¹⁶⁾J. Schreyer, G. Thompson and L. Ockerman, Analytical Chem., 22, 1426 (1950).

NaOH, 1 ml of chromic chloride solution (1.7 gm CrCl₃/100 ml) and 5 ml H₂O were added. Any ferrate introduced into this solution reacts with Cr³⁺ to form chromate in accord with:



The corresponding chromate was analyzed by diluting the solution to 50 ml, taking a 10 ml aliquot, diluting this to 15 ml and carefully adding H₂SO₄ to pH 8 or 9. Ferric hydroxide was centrifuged off, and the solution then acidified with 2 ml of 5 N H₂SO₄. On dilution to 40 ml, 2 ml of di-phenyl carbazide reagent were added, dilution carried to 50 ml, and the violet color as developed by dichromate was compared with suitable standards using the electrophotometer.

A coiled Armco iron specimen of 60 cm² area and suspended from a glass hook was passivated in concentrated nitric acid, and carefully washed in one or more beakers of distilled water without destroying passivity. The coil was then plunged into the above-described NaOH solution containing Cr³⁺ and allowed to remain about 10 min., after which analysis of the alkaline solution was carried out for CrO₄⁻⁻. Blank determinations using the identical procedure were run with platinum sheet having the same area as iron. Chromates were found over and above small blank corrections, indicating that ferrate or an

analogous compound is formed when iron reacts with concentrated nitric acid. A summary of results is given in Table IV. The data show that reproducibility, typical of most experiments in passivity, was not good, but nevertheless was adequate to prove the point. The amount of ferrate corresponding to the analyzed chromate appeared to be independent of whether one or three washes were employed, which may be taken as further evidence that the compound is chemisorbed on iron.

The variable amounts of ferrate may indicate partial decomposition taking place during washing and at the time of immersing the iron specimen into NaOH. Some specimens may have lost most of their passivity, judging by the amount of ferrate found and that produced by a specimen known to be active. Any nitrate or nitrite carried over on the passive iron surface could not have oxidized Cr^{3+} to CrO_4^{--} , because a check run showed that 100 mg KNO_3 or KNO_2 added to the NaOH solution containing Cr^{3+} did not produce chromate in excess of the normal blank. Moles of iron far in excess of moles of ferrate originated probably through carry-over of ferric nitrate and by corrosion of the iron specimen by an adhering film of acid not easily removed by washing. Data of Table IV show that additional water washes removed more of the residual acid solution, and thereby also reduced the amount of iron in the NaOH wash. It is questionable whether all the adhering solution can be removed without destroying passivity. Because of these factors, a more precise analysis of the surface compound responsible for passivity was not attempted.

Discussion

The experimental evidence can be interpreted, accordingly, in terms of a hexavalent iron compound, related to or identical with

ferric acid, H_2FeO_4 , which forms at the anode areas as a result of intense local action galvanic currents when iron reacts with concentrated nitric acid. The compound in part appears to be chemisorbed on the metal surface simultaneous with its formation. According to Bonhoeffer⁽²⁾ and Vetter⁽¹⁷⁾, local action currents increase with accumulation of nitric

⁽¹⁷⁾K. Bonhoeffer and K. Vetter, Z. Physik. Chem., 193, 127 (1950).

acid reduction products, in particular HNO_2 , which act as cathodic depolarizers, the anodic current density eventually reaching the critical value for anodic passivation. Franck's⁽¹⁸⁾ measurements of anodic

⁽¹⁸⁾U. Franck, Z. f. Naturforschung, 4a, 383 (1949).

passivation of iron in dilute H_2SO_4 showed that the critical value may be about 17 amperes/cm². Anodic polarization of this magnitude suffices to produce ferrate or its analog either in situ, or in high concentrations at anodic regions. The compound upon chemisorbing on iron is more stable chemically than in the free state. Chemical stabilization of the passive film by adsorption was suggested earlier by Bennett and Burnham⁽¹⁹⁾ and by Bancroft and Porter⁽²⁰⁾ who considered that adsorbed

⁽¹⁹⁾C. Bennett and W. Burnham, Trans. Electrochem. Soc., 29, 217 (1916).

⁽²⁰⁾W. Bancroft and J. Porter, J. Phys. Chem., 40, 37 (1936).

metastable FeO_3 was responsible for passivity.

The chemisorbed compound, according to our viewpoint, satisfies surface affinities of iron, and thereby reduces tendency of the metal surface to react, making it passive in the same sense as chromates are

TABLE IV

ANALYSES OF PASSIVE FILM ON IRON FOR FERRATES AND IRON CONTENT

No. of washes in water	micrograms CrO ₄ ⁻⁻ Formed on Immersion in NaOH + Cr ⁺⁺⁺ Solution*		micrograms Fe in NaOH + Cr ⁺⁺⁺ Solution**		Equivalent micromoles/cm ²	
					FeO ₄ ⁻⁻	Fe
1	138		1750		0.020	0.52
1	31		1310		0.005	0.39
1	57		1230		0.008	0.37
1	82		1580		0.012	0.47
2	89		1100		0.013	0.33
2	125		780		0.018	0.23
3	34		360		0.005	0.11
3	109		490		0.016	0.15
3	20		---		0.003	---
3***	10		80		0.001	0.02

*Corrected for blank equal to 24 micrograms CrO₄⁻⁻.

**Corrected for blank equal to 120 micrograms Fe.

***Passivity intentionally destroyed by striking specimen on side of beaker in second wash.

thought to cause passivity when chemisorbed on iron^(12,13,21,22,23), or

(21) H. H. Uhlig, J. Electrochem. Soc., 97, 215C (1950).

(22) "Metal Surface Phenomena", H. H. Uhlig, chapter of "Metal Interfaces", pp. 312-35, A.S.M., Cleveland (1952).

(23) H. H. Uhlig, Annals N.Y. Academy of Sciences, 58, 843-54 (1954).

oxygen when chemisorbed on the stainless steels^(12,21,22,23,24).

(24) G. Tammann, Z. Anorg. u. Allg. Chem., 107, 104, 236 (1919).

In this connection, it may be significant that the maximum amount of ferrate released from passive iron is approximately 2×10^{-8} mole/cm² of geometric surface (Table IV). Geary⁽²⁵⁾ found a comparable amount

(25) Ref. 12, p. 221.

of chromate to adsorb on oxide-free iron from 0.001 M chromate solution, namely, 5×10^{-8} mole/cm² geometric surface. Powers and Hackerman's⁽¹⁵⁾ data for air-exposed iron correspond to 0.9×10^{-8} mole/cm², as do data of Brasher and Stove⁽¹⁴⁾.

No iron reacts with nitric acid if iron is pre-exposed to ferrates or to chromates, because the surface is already covered with a passive film of the same kind as forms by reaction of acid with iron. At the same time, ferrate or its analog adsorbed on iron, no longer has the same affinity for its external environment because of chemical attachment to the metal lattice underneath, and it is, therefore, relatively more

stable with respect to acids, hydrogen peroxide, nitrous acid and other reagents with which it normally reacts when in the free state.

High anodic local action current densities necessary for passivation are favored by adsorbed oxygen on iron, both because oxygen forms effective cathodic surfaces, and because local action currents are confined to smaller exposed anodic areas. Hence, less iron reacts with HNO_3 if the iron is pre-exposed to air. Pre-exposure to carbon monoxide similarly aids passivation through increased cathodic surface of adsorbed CO, similar to the behavior of adsorbed oxygen. At such time as the hexavalent iron compound forms an adsorbed layer or layers, the compound thereafter is continuously renewed at incipient small anode areas by continuing local action currents. The measured corrosion rate of passive iron in unstirred concentrated HNO_3 after several hours immersion was found equal to about 20 mdd, which is equivalent to a total corrosion current ($\text{Fe} \longrightarrow \text{Fe}^{+++} + 3\text{e}$) of 12 $\mu\text{amp}/\text{cm}^2$. At exposed anodes, of course, the current density is much higher. If 17 amp/cm^2 is necessary to achieve passivity, as Franck indicated, the ratio of anode to cathode area is $\frac{12 \times 10^{-6}}{17}$ or 7×10^{-7} . Vetter⁽¹⁰⁾, using corrosion rates of iron in stirred concentrated HNO_3 containing 2% urea, similarly calculated the ratio to be 30×10^{-7} . Both values indicate that practically all the surface is cathode, a very small portion of which at any moment acts as anode.

Repair of the adsorbed film of compound occurs even in relatively dilute nitric acid. The lower conductivity and limited oxidizing properties of the dilute acid, together with a correspondingly large anodic area of iron when first immersed, are not sufficient to induce

passivity. But when passivity is previously induced by immersion of iron into concentrated HNO_3 , corrosion currents in dilute acid are entirely adequate for maintaining passivity.

So long as the compound remains on the surface and is repaired by local action currents, the specimen remains passive. Of course, if the metastable compound is broken down over more than a small region by mechanical action or heat, ensuing galvanic action of the induced anode in contact with a large area of cathode differing in potential by as much as 0.9 volt (the potential difference between passive and active iron in water) is sufficient to cathodically reduce the compound at adjoining areas of the surface. This action is observed by a rapidly moving front of non-passive iron increasing in area as more and more of the surface is activated. Bonhoeffer^(2,26) and his co-workers^(17,18)

⁽²⁶⁾K. Bonhoeffer, J. Gen. Physiology, 32, No. 1, 69 (1948).

have studied in detail the mechanism of propagation of active-passive fronts as a model for nerve impulse propagation, following the earlier studies of passivity in this relation by Heathcote⁽²⁷⁾ and by Lillie⁽²⁸⁾.

⁽²⁷⁾H. Heathcote, Z. Physik. Chem., 37, 368 (1902); J. Soc. Chem. Ind., 26, 899 (1907).

⁽²⁸⁾R. L. Lillie, Biol. Rev., 11, 181 (1936).

Admission of halogen ions quickly breaks down passivity, possibly because these ions compete with the passivating compound for sites on the iron surface. Chloride ions adsorbed on iron have very short life

(small activation energy for reaction), contact with the surface being followed by rapid hydration and solution of metal ions. Such areas become anodes with subsequent progressive breakdown of passivity by electrolytic action as noted above. It is also possible that chloride ions hasten reduction of the surface iron compound by reaction to form chlorine, or by some other mechanism.

Our conclusion that ferric acid or a related compound is responsible for passivity agrees with the deductions of Bonhoeffer, who suggested that the "oxide film" on iron passivated in nitric acid must have a higher oxygen dissociation pressure than any known normal oxide^(2,29).

⁽²⁹⁾K. Bonhoeffer, Z. Elektrochem., 47, 147 (1941).

Ferric acid certainly fits into this category. It also agrees with the previous proposal of Bennett and Burnham⁽¹⁹⁾ and of Bancroft and Porter⁽²⁰⁾ that a higher oxide FeO_3 appears to be necessary to explain their passivation experiments and potential measurements. The present work shows indeed that an unstable, higher oxide exists. Our work does not support the proposal of Vetter⁽³⁰⁾ that a common oxide of iron

⁽³⁰⁾K. Vetter, Z. für Physik. Chem., 202, 1 (1953).

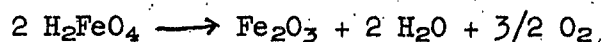
unsatisfied in composition with respect to its environment covers the surface, since such an oxide would not account for hexavalent iron or a structure analogous to the chromates.

Some investigators have concluded that the passive film on iron is a physical barrier layer consisting of Fe_2O_3 ^(31,32). Support for

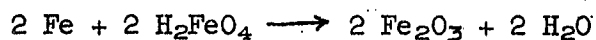
(31) "Protective Films on Metals", E. S. Hedges, p. 114, Chapman and Hall (London) 1937.

(32) U. R. Evans, Trans. Faraday Soc., 40, 120 (1944).

this assumption was obtained in part by isolating an oxide film of the composition Fe_2O_3 using the iodine reaction or anodic dissolution techniques. However, an isolated film of Fe_2O_3 , according to the present discussion, is merely an end product of the metastable hexavalent compound, and probably plays a small part, if any, in the passivation phenomenon. Ferric acid, for example, may decompose as follows:



or



On this basis, the maximum amount of ferrate found per apparent square centimeter of passive surface (2×10^{-8} mole/cm², Table IV) decomposes to a residual film of Fe_2O_3 ($d = 5.12$) 125 Å thick. The corresponding thickness, based on a reasonable roughness factor of 2 or 3, is 40 to 60 Å. These values agree approximately with optically determined values of 25 to 100 Å for the primary film reported by Tronstad and Borgmann⁽³³⁾, and with thicknesses for the decomposed

(33) L. Tronstad and C. Borgmann, Trans. Faraday Soc., 30, 349 (1934).

primary film of 78 Å by microbalance weighings of Gulbransen⁽³⁴⁾, and with

⁽³⁴⁾E. A. Gulbransen, Trans. Electrochem. Soc., 82, 375 (1942).

80 Å by dissolution of oxide in acid as reported by W. Schwarz⁽³⁵⁾. The

⁽³⁵⁾W. Schwarz, Z. Elektrochem., 55, 170 (1951).

values are somewhat higher than 23 Å calculated by Vetter⁽³⁶⁾ from the

⁽³⁶⁾K. J. Vetter, Z. Elektrochem., 55, 683 (1951).

amount of electricity required to reduce the passive film.

An explanation is still required for the function of urea and hydrogen peroxide in the passivation phenomena. In accord with the function of HNO_2 as depolarizer, enough iron must first react with nitric acid to produce a high concentration of nitrous acid near the metal sufficient for effective cathodic depolarization and corresponding achievement of the critical anodic current density for passivity. Consequently, if nitrous acid is added beforehand, as when potassium nitrite is added to nitric acid, iron becomes passive with much less than the normal amount of iron reacting. Urea destroys nitrous acid, but the reaction is not sufficiently rapid, as Vetter showed⁽¹⁰⁾, to prevent build-up of nitrous acid at the metal surface by the iron-nitric acid reaction. Hence, approximately the normal amount of iron reacts with nitric acid plus urea to produce passivity, as the foregoing experiments show. After passivation, urea apparently succeeds in reducing the prevailing HNO_2 concentration at the surface and reduces

the corresponding local action currents, thereby preventing repair of the adsorbed film, and causing loss of passivity, but only momentarily because when larger anode areas form, nitric acid is more rapidly reduced at adjacent cathodes, HNO_2 again forms in greater concentration, and local action currents increase, followed by recovery of passivity. This situation accounts for periodic active-passive phenomena when iron is immersed in HNO_3 -urea mixtures.

Hydrogen peroxide apparently reduces the concentration of nitrous acid by oxidizing it to nitric acid⁽³⁷⁾. It may also act to reduce

⁽³⁷⁾Ref. 9, p. 685.

ferric acid in the same manner it reduces chromates. Hence, periodic breakdown of passivity occurs, and more iron reacts during the two-minute immersion in concentrated HNO_3 containing H_2O_2 .

As mentioned before, the metastable compound after adsorption on passive iron is not as easily reduced as properties of ferrates otherwise suggest, in the same sense that chemisorbed oxygen on tungsten is not easily reduced by hydrogen at elevated temperatures⁽³⁸⁾. Through

⁽³⁸⁾I. Langmuir, J.A.C.S., 38, 2221 (1916).

chemisorption, both the metal and the adsorbate are passive to their environment, until such time as localized breakdown occurs in some portion of the passive film.

ACKNOWLEDGMENT

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